

Measurement of the kinetic mobility in a stratifying liquid solution by the optical method

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(Submitted 24 September 1984)

Pis'ma Zh. Eksp. Teor. Fiz. **40**, No. 9, 389–391 (10 November 1984)

Nonlinear concentration refraction of light in a binary liquid solution (nitromethane–*n*-amyl-alcohol) has been observed for the first time. The range of variation of the macroscopic mobility is estimated from the experimental results, independently of other kinetic parameters.

1. The kinetics of binary solutions in the linear Onsager approximation is determined (in combination with the coefficients of thermal conductivity and thermal diffusion) by the coefficient of kinetic mobility L , which relates the mass flow to the chemical-potential gradient μ . The quantity L has still not been measured directly (more precisely, it has not been measured other than in combination with some other critical parameter) for any solution. A simple analysis of the diffusion equation shows that this measurement can be performed only in the presence of strong external perturbations. It has been suggested that intense light¹ or sound² beams be used for this purpose. The implementation of the method proposed in Ref. 1 for determining the value of L experimentally from the parameters of the concentration optical self-effect is described below.

2. In the experiment performed using the arrangement shown in Fig. 1, radiation from a ruby laser RL (single-mode free-lasing regime; pulse energy $E = 0.7$ J with a pulse duration of $\tau = 1$ ms) was focused by a lens L into the cell C with a critical mixture of nitromethane (0.61 molar fraction) and *n*-amyl-alcohol. The change in the refraction of the light beam as a function of the temperature of the solution and the energy density of the incident beam was determined from measurements of the width of the transverse intensity distribution in the two planes E_1 and E_2 . The solution cell

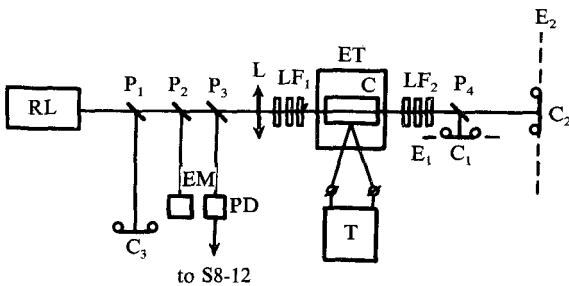


FIG. 1. Experimental arrangement. RL is the ruby laser, $P_{1,4}$ are the beam-splitting plates, $C_{1,3}$ are cameras, EM is an energy meter, PD is a LFD-2 photodiode, L is a lens, $LF_{1,2}$ are light filters, ET is an electronic thermostat, C is the cell with the solution, and T is a thermometer.

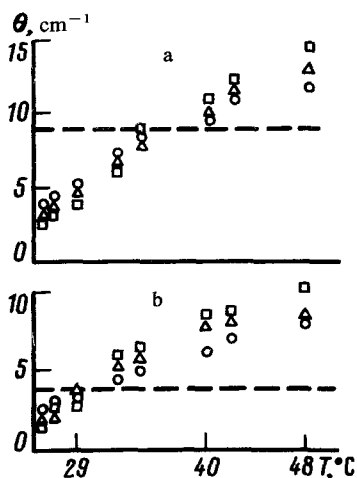


FIG. 2. Temperature dependence of the inverse beam width in the E_1 plane. The focal length of the lens is $F = 100$ cm (a) and 50 cm (b). The energy of the laser pulse is $E = 0.7$ J (\square); 0.4 J (\triangle); and 0.28 J (\circ).

was placed inside the cell of an electronic thermostat; the temperature was stabilized in the range from 27 to 48 °C (the critical stratification temperature is $T_c = 26.7$ °C) to within $\pm 10^{-3}$. A thermistor calibrated to within $\pm 10^{-4}$ was used for the temperature measurements and for additional monitoring of the temperature stabilization. The energy density of the incident beam was varied by using appropriate light filters and lenses. The measurements of the quantity $\theta = (2a_e)^{-1}$ ($2a_e$ is the width of the beam at the one-half intensity level) in the plane E_1 are shown in Fig. 2. The broken horizontal lines in the figure mark the values of θ in a weak field (linear diffraction divergence). Far from the critical point ($T > 33$ °C), the nonlinearity moves the focal point away from the input face of the cell. Here the thermal defocusing lens is effective; the degree of nonlinear defocusing decreases as the temperature approaches T_c , primarily due to the increase in the heat capacity C_p . At the same time, the contribution of the constantly focusing nonlinear concentration mechanism increases.¹ At temperatures $T < 33$ °C, we see a strictly concentration self-focusing, which intensifies as $T \rightarrow T_c$ due to the increase of L . The slope of $\theta(T)$ increases at high intensities; the behavior of the curves changes as the focal length of the lens L is varied, indicating that the concentration mechanism is responsible for this effect (the nonlinear focal length is proportional to the energy density W in the pulse, whereas the total energy is the predominant parameter of the thermal lens).

3. The experimental results were analyzed by making use of the theory of concentration self-focusing¹ in the standard aberration-free approximation,³ in which the thermal prefocusing was taken into account. Furthermore, because of the slow rate of both of these processes, $\tau_c > \tau_T > \tau$ (the time required for establishing the concentration nonlinearity is $\tau_c \sim a^2/D \sim 10^2$ s, D is the diffusion coefficient, $\tau_T \sim a^2/\chi \sim 10$ s, χ is the thermal diffusivity, and a is the radius of the beam in the plane of the lens), we assumed in the calculation that the pulse is delta-shaped. The only parameter describing refraction is the difference

$$\alpha = (E/E_T) - (W/W_c). \quad (1)$$

Here E_T and W_c are the parameters characterizing the thermal and concentration mechanisms for the nonlinearity,

$$E_T = n\rho c_p \lambda^2 / 8\pi\delta |\partial n / \partial T|, \text{ and } W_c = cn\rho^2 \lambda^2 / 8\pi L (\partial n / \partial c)^2, \quad (2)$$

where n is the index of refraction of the solution, ρ is the density, λ is the wavelength, and δ is the absorption coefficient. Comparison of the data for $\alpha(T, E)$ for two values of a (lenses with a focal length $F = 50$ and 100 cm) made it possible to determine $E_T(T)$ and $W_c(T)$ separately. The "thermal energy" E_T increases monotonically from 0.02 J ($T = 48^\circ\text{C}$) to 0.03 J ($T = 27.5^\circ\text{C}$). The corresponding values of W_c decrease from 10.0 to 4.6 J \cdot cm $^{-2}$, in agreement with the general tendency for L to increase as $T \rightarrow T_c$.

4. The data on the parameters (even the noncritical parameters) of this particular solution are incomplete (see Ref. 4). Substituting the values calculated in Ref. 2 in the crudest additive model $n = 1.39$, $\rho = 1.01$ g \cdot cm $^{-3}$, and $\partial n / \partial c = 0.02$ (this quantity can also be of the order of unity; correspondingly, the estimate of L is greatly exaggerated), we obtain $L = (1.4-0.6) \times 10^{-4}$ g \cdot s/cm 3 in the indicated temperature range. This value is much higher than the mobility in ideal solutions: $L_n \sim 10^{-12}$ g \cdot s/cm 3 . The latter estimate, which is strictly correct, however, only for solutions of isotopes, gives only a lower bound for L . Our experimental estimate of L , which must of course be refined (the noncritical parameters used in Ref. 2 must be measured at the same time and the statistical base of optical measurements must be enlarged), shows that the value of L in stratifying solutions can be much higher than the ideal asymptotic value even under noncritical conditions (we recall that $L \rightarrow \infty$ as $T \rightarrow T_c$).

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⁴A. Weisberger *et al.*, *Organicheskie rastvoriteli* (Organic Solvents), *Inostr. Lit.*, Moscow, 1958.

Translated by M. E. Alferieff

Edited by S. J. Amoretty